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Note

Organophosphorus liquid phases: Characterization and application to the gas chromatographic analysis of organophosphorus compounds

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Gas-liquid chromatography is a separation technique whose versatility has been largely attributable to the wide selection of phases available. This great number of compounds has created some problems for the chromatographer, especially regarding the choice of selective liquid phases. A solution to this problem is the design, or the choice, of a liquid coating with a chemical structure with the features that contribute to chemical specificity.

In our previous organophosphorus chemistry studies¹⁻⁴, the need was observed to obtain selective gas chromatographic (GC) separations of organic samples containing phosphorus. Except in the field of pesticide residues, little has been reported previously on the GC analysis of organophosphorus intermediates and products. On the other hand, the columns used include conventional and general-purpose phases. Phosphates have been determined on Carbowax 20M (ref. 5), silicone SE-30 (refs. 6, 7) and Apiezon N (ref. 8); phosphites on silicone UC-W98 (ref. 9); phosphines on DC high-vacuum grease and Reoplex 400 (ref. 10); pyrophosphates on SE-30 (ref. 11); diaryl phosphochloridates on Carbowax 20M (ref. 11); and derivatives of alkylphosphonates on SE-30 and OV-17 (ref. 12).

A series of acidic and neutral organophosphorus compounds have previously been examined as liquid phases, in order to determine the relationship between their physical properties and the retention times of various compounds¹³. Their application to the resolution of mixtures of organophosphorus compounds was not evaluated.

The purpose of this work was to characterize non-volatile phosphites, distearyl pentaerythrytol diphosphite (DPD) and tetrakis(nonylphenyl)polypropylene glycol 425 diphosphite (TPD) (Weston Chemical, U.S. Patents 3,047,608 and 3,205,269), in order to permit the use of these products as liquid coatings for the separation of organophosphorus compounds.

EXPERIMENTAL

Reagents and materials

The organophosphorus compounds used in this work were obtained from the following sources: DPD, TPD and diallyl phosphite from Weston Chemical (U.S.A.), dimethyl and diethyl phosphite from Schuchardt (Munich, G.F.R.), diisopropyl

phosphite, triethyl phosphate, triethyl thiophosphate and trimethyl phosphate from Aldrich (Milwaukee, Wisc., U.S.A.) and dibutyl phosphite from Mobil Chemical (U.S.A.).

Chromatographic materials, Varaport 30 (100–120 mesh) and squalane were acquired from Varian Aerograph (Palo Alto, Calif., U.S.A.) and the kit for determining the McReynolds constants from Supelco (Bellefonte, Pa., U.S.A.).

Instrumental conditions

All chromatographic data were collected on a Varian Aerograph 1522-B gas chromatograph using a flame ionization detector with a hydrogen flow-rate of 30 ml/min and an air flow-rate of 300 ml/min. Nitrogen was employed as the carrier gas, with a flow-rate of 25 ml/min. The recorder was a Varian Model A-25.

Column preparation

The support (Varaport 30, 100–120 mesh) was coated by evaporation of a methylene chloride solution of the organophosphorus phases using a rotary evaporator. The last traces of solvent were removed by pan drying in an oven at 100°. The columns were made of 1/8-in. O.D. stainless steel or Pyrex glass. The columns were conditioned for 12 h at 150° for TPD and at 130° for DPD.

Thermal stabilities

Thermal stabilities of the stationary phases were determined by thermogravimetric analysis (TGA), with a Netzch thermobalance (Gerätebau GmbH, Selb/Bay., G.F.R.), and by column bleeding as indicated by the chromatographic base-line stability.

RESULTS AND DISCUSSION

The most significant physical property of the coating material to the chromatographer is the volatility (or pyrolysis temperature). The TGA plot (Fig. 1) is

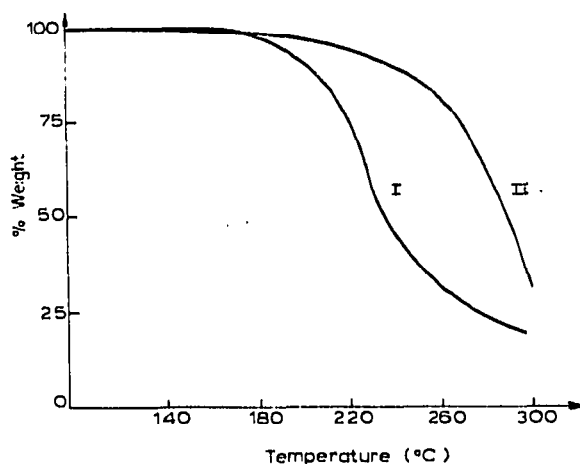


Fig. 1. Thermogravimetric analysis of TPD (I) and DPD (II).

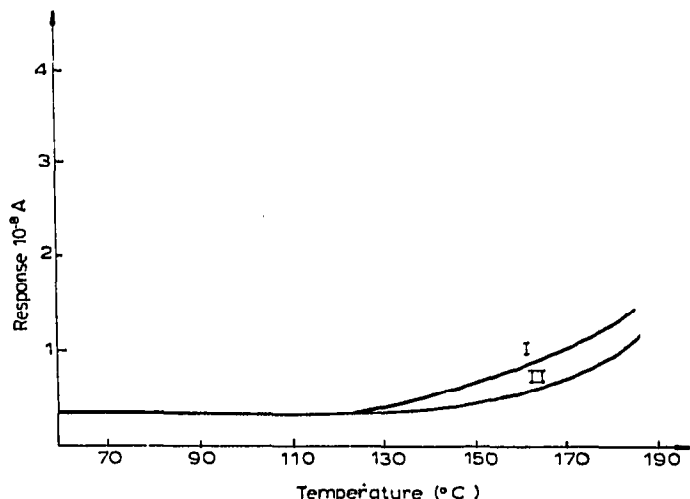


Fig. 2. Detector response to column bleeding: I, 5% TPD; II, 5% DPD.

indicative of the useful temperature range that one may expect of the phases. The weight loss curve shows no volatilization below 130° for DPD or below 150° for TPD.

In order to test the chromatographic thermal performance under practical conditions, the flame detector response to column bleeding was measured by recording the base-line while the oven was programmed from 50 to 200° at $4^{\circ}/\text{min}$ (Fig. 2). The bleeding level and the TGA results show that DPD begins to become inefficient above 130° and TPD above 150° .

For the chromatographic characteristics of the phases, polarities were determined. There have been several attempts to describe the polarity of a stationary phase, and the most useful method yet reported is the McReynolds system¹⁴ based on the Rohrschneider classification¹⁵. The McReynolds constants were calculated at 50° and 100° for DPD and TPD (Table I). For DPD, the constants indicate that the

TABLE I

ΔI VALUES RELATIVE TO SQUALANE (McREYNOLDS CONSTANTS)

ΔI = Variation of retention index with respect to a squalane column for: a, benzene; b, 1-butanol; c, 2-pentanone; d, nitropropane; e, pyridine; f, 2-methyl-2-pentanol; g, 1-iodobutane; h, 2-octyne; i, 1,4-dioxane; j, *cis*-hydridane.

Phase	Column temperature ($^{\circ}\text{C}$) [*]	ΔI									
		a	b	c	d	e ^{**}	f	g	h	i	j
DPD	50	57	226	31	92	130	130	52	52	57	18
DPD	100	67	219	92	164	158	161	61	36	10	17
TPD	50	204	438	186	307	404	350	146	119	239	58
TPD	100	177	462	272	398	495	322	153	118	186	69

^{*} McReynolds used a temperature of 120° , but we found that the standards eluted too rapidly from the organophosphorus liquid phases at this temperature.

^{**} Peak tailed.

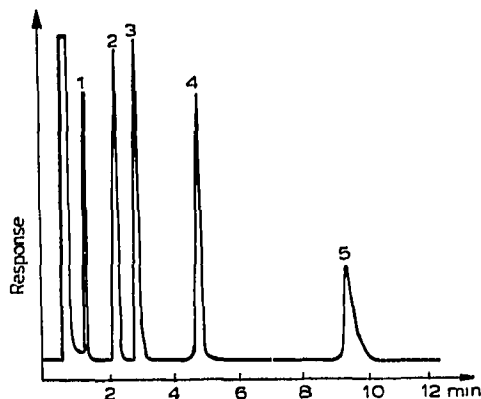


Fig. 3. Analysis of aliphatic diphosphites on DPD. Column, Pyrex; 10% DPD; 75–125° at 4°/min, then isothermal. 1 = Dimethyl; 2 = diethyl; 3 = diisopropyl; 4 = diallyl; 5 = dibutyl.

polarity is similar to that of Ucon 50 HB-280X, and less than for TPD, which is similar to diethylene glycol stearate (except ΔI for 1,4-dioxane).

Regarding applications to chemical problems, a variety of organophosphorus compounds have been chromatographed successfully using the novel phases. Figs. 3 and 4 show the efficient separation of several aliphatic phosphites using both phases.

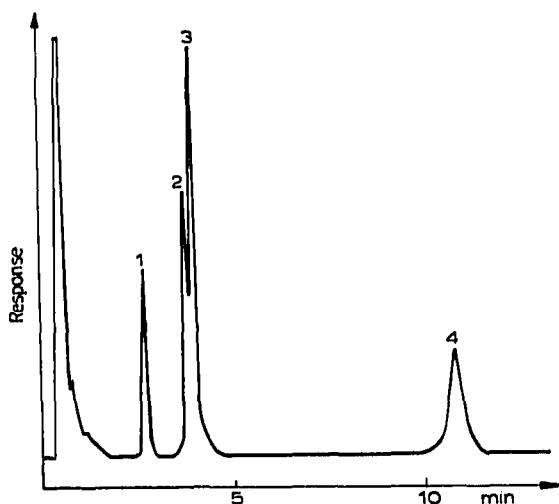


Fig. 4. Analysis of aliphatic diphosphites on TPD. Column, Pyrex; 10% TPD; 80–125° at 4°/min, then isothermal. 1 = Dimethyl; 2 = diethyl; 3 = diisopropyl; 4 = dibutyl.

The difficult resolution of thiophosphates and analogous phosphates was obtained for DPD and TPD for the specific case of triethyl thiophosphate and triethyl phosphate, correct separation factors being obtained (Figs. 5 and 6).

The coatings studied have demonstrated high selectivity for organophosphorus compounds and therefore may be useful in gas chromatographic analysis.

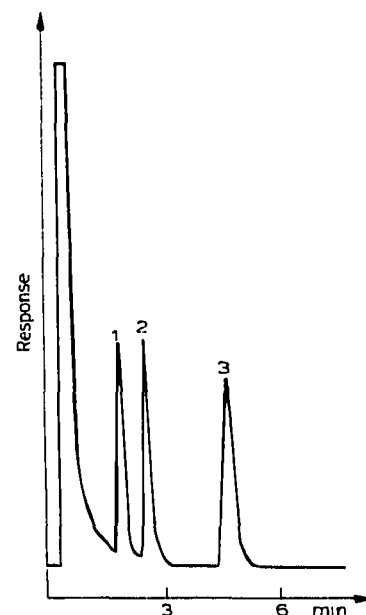
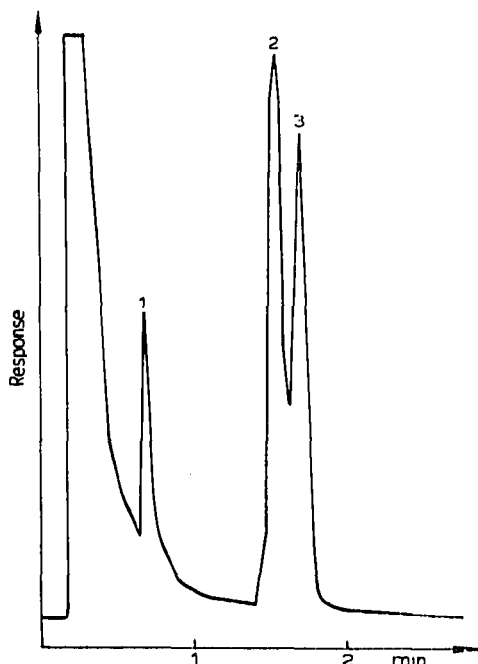


Fig. 5. Analysis of phosphates on DPD. Column, Pyrex; 10% DPD; 125°, isothermal. 1 = Trimethyl phosphate; 2 = triethyl thiophosphate; 3 = triethyl phosphate.

Fig. 6. Analysis of phosphates on TPD. Column, Pyrex; 10% TPD; 115°, isothermal. 1 = Triethyl thiophosphate; 2 = trimethyl phosphate; 3 = triethyl phosphate.

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